

AD743135

Order No. 1479

Order Code 1820

Contract No. N00014-69-A0200-6018

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Name of Contractor:

Regents of the University of California

Project and Grant Officer

Building 504, Matthews Campus

University of California, San Diego

La Jolla, California 92037

Short Title of Work:

Optimized Cluster Expansion for  
Classical Fluids. III. Applications  
to Ionic Solutions and Simple  
Liquids

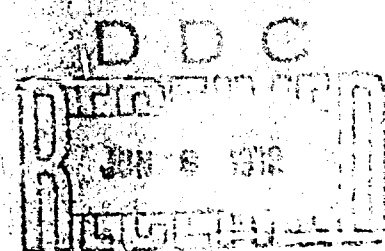
Effective Date of Contract:

1 August 1968

To: 31 July 1972

Amount of Contract: \$120,000

Sponsored by  
Advanced Research Projects Agency  
ARPA Order No. 1479



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## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Department of Chemistry University of California, San Diego La Jolla, California 92037		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Optimized Cluster Expansions for Classical Fluids. III. Applications to Ionic Solutions and Simple Liquids			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name) Hans C. Andersen, David Chandler and John D. Weeks			
6. REPORT DATE May 23, 1972		7a. TOTAL NO. OF PAGES 21	7b. NO. OF REFS 17
8a. CONTRACT OR GRANT NO. N00014-69-A-0200-6018		9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 13	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) ARPA Order No. 1479	
c.			
d.			
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Office of Naval Research Physics Branch Washington, D. C. 20360	
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UNCLASSIFIED

Security Classification

14.

KEY WORDS

LINK A

LINK B

LINK C

ROLE

WT

ROLE

WT

ROLE

WT

Optimized Cluster Expansions for Classical Fluids. III.  
Applications to Ionic Solutions and Simple Liquids\*

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### Abstract

In a previous paper we have derived a number of simple approximations for the thermodynamic and structural properties of liquids. Here we test these approximations by applying them to models for ionic solutions and atomic liquids and comparing the results with those obtained from Monte Carlo and molecular dynamics simulations. In particular, the pair-correlation functions for 1-1 primitive model aqueous ionic solutions are calculated using the EXP approximation. The internal energy for 2-2 salts is obtained from the ORPA +  $B_2$  approximation. The pair-correlation function for the Lennard-Jones fluid is calculated with the EXP approximation. In all cases the results obtained agree closely with those obtained from computer experiments. Thus, the ORPA +  $B_2$  approximation for the free energy and the EXP approximation for the pair correlation function provide a theory that is both very accurate and applicable to a wide variety of classical fluids.

## I. Introduction

This paper is the third in a series concerning optimized cluster expansions for equilibrium classical fluids. The first article<sup>1</sup> (I), presents general graphical methods and some simple approximations for describing fluids composed of spherical particles. The second<sup>2</sup> (II) generalizes the methods to apply to molecular fluids. The object of this third article is the study of the accuracy of the methods. In particular, we apply the ORPA +  $B_2$  approximation for the free energy [Eq. (5.5) of I] and the EXP approximation for pair-correlation functions [Eq. (5.7) of I] to two different model fluids. These approximations are the principal results of paper I. Their molecular analogs are the principal results of paper II.

In Section II, we study the primitive model electrolytes for 1-1 and 2-2 aqueous ionic solutions. The pair-correlation function is computed for 1-1 salts using the EXP approximation. The internal energy for 2-2 salts is obtained from the ORPA +  $B_2$  approximation. The calculated results agree closely with those obtained from Monte Carlo computer experiments.

The pair-correlation function for simple liquids is studied in Section III. The EXP approximation is used to calculate  $g(r)$  for the Lennard-Jones fluid. The results obtained agree virtually perfectly with those obtained from molecular dynamics computer experiments.

Some concluding remarks are made in Section IV.

Throughout the paper, the notation and terminology is the same as that used in I.

## II. Ionic Solutions

In this section, we consider the symmetric primitive model for aqueous ionic solutions which represents solvated ions as charged hard spheres. The cations and anions have the same hard sphere diameter,  $d$ , and the same magnitude of charge,  $ze$ , where  $e$  is the magnitude of the electronic charge. We let the subscripts 1 and 2 denote anions and cations, respectively. Then the pair interaction<sup>3</sup> between an ion of type  $\alpha$  and an ion of type  $\gamma$  is  $u_d(r) + u_{\alpha\gamma}(r)$ , where  $u_d(r)$  is the hard core potential (the reference interaction),

$$\begin{aligned} u_d(r) &= \infty, & r < d, \\ &= 0, & r \geq d, \end{aligned} \quad (2.1)$$

and  $u_{\alpha\gamma}(r)$  is the perturbation

$$u_{\alpha\gamma}(r) = z_\alpha z_\gamma e^2 / \epsilon r, \quad r \geq d. \quad (2.2)$$

Here,  $z_\alpha = (-1)^\alpha z$ , and  $\epsilon$  is the dielectric constant of the solvent.

The number densities,  $\rho_1$  and  $\rho_2$ , of the two ions are equal because of electroneutrality.

The perturbation potential,  $u_{\alpha\gamma}(r)$ , can be chosen arbitrarily for  $r \leq d$  without changing the physical properties of the model fluid. The particular functional form we adopt for  $u_{\alpha\gamma}(r)$  in this region is the one which satisfies the optimization condition discussed in I and which hence improves the accuracy of truncated cluster expansions.

Monte Carlo computer experiments have been performed by Card and Valleau<sup>4</sup> for primitive model electrolytes which simulate aqueous ionic solutions of 1-1 (i.e.,  $z=1$ ) and 2-2 ( $z=2$ ) salts. We report below results obtained when the EXP and ORPA + B<sub>2</sub> approximations are applied to these same models.

The salt concentrations for which the computer experiments have been performed are sufficiently small that the Percus-Yevick (PY) theory for the hard sphere reference system can be used without loss of accuracy. When the PY theory is used, the solution of the variational problem which gives the optimized  $u_{\alpha\gamma}(r)$  for  $r \leq d$  [Eq. (4.1') of I] is equivalent to the solution of the mean-spherical model (MSM) equation for the fluid.<sup>5</sup> Walsman and Lebowitz<sup>6</sup> have solved this problem analytically for the symmetric primitive model. With their solution, one finds that

$$u_{\alpha\gamma}(r) = (z_{\alpha} z_{\gamma} e^2 / Dd) (2B - B^2 r/d), \quad r \leq d, \quad (2.3)$$

and

$$a_{\text{RING}} = (12\pi d^3)^{-1} [6x + 3x^2 + 2 - 2(1+2x)^{3/2}]. \quad (2.4)$$

In these equations,

$$x = \kappa d = [8\pi z^2 e^2 c / k_B T \epsilon]^{1/2} \quad (2.5)$$

$$B = x^{-2} [x^2 + x - x(1+2x)^{1/2}], \quad (2.6)$$

where  $c = \rho_1 = \rho_2$  is the salt concentration. The quantity  $\kappa$  is the familiar Debye inverse screening length.

Using Eqs. (2.4) and (2.3), it is a straightforward calculation to apply the ORPA +  $B_2$  approximation [Eq. (5.5) of I] and the EXP approximation [Eq. (5.7) of I] and compare the results with those obtained from Monte Carlo simulations<sup>4</sup> of ionic solutions. Figures 1 and 2 show the pair correlation functions for 1-1 salts for concentrations between .009 and 2 M. In Table I, the contact values of the pair correlation function are given for these solutions. For 2-2 salts, the configurational energy is shown in Table II. In all these cases



the agreement between the two methods is quite good. The energy results for 2-2 salts are particularly interesting since they exhibit the rapid convergence of the optimized cluster expansion. Note that the perturbation in this case is not small. At hard core contact,  $|u_{\alpha\gamma}(r)|$  is greater than  $6 k_B T$ !

It should be noted that although the solution of the MSM equations is used to obtain the optimized renormalized potential, the results of the ORPA +  $B_2$  and the EXP approximations are not the same as those of the MSM equation.<sup>7</sup> For 1-1 and 2-2 salts, the MSM predictions for the internal energy disagree significantly with those of the Monte Carlo and ORPA +  $B_2$  calculations (see Table II). The disagreement is especially striking at very low concentrations. The reason for the disagreement is that the MSM is qualitatively incorrect at low concentrations. The correct low density limit for  $g_{\alpha\gamma}(r)$  is  $\exp[-u_{\alpha\gamma}(r)/k_B T]$  for  $r \geq d_{\alpha\gamma}$ . The MSM equation, however, gives  $1 - u_{\alpha\gamma}(r)/k_B T$ . In fact, the MSM result (for the 1-1 and 2-2 salts studied in this section) has the unphysical feature that  $g_{\alpha\alpha}(r)$  is negative for distances at and near contact of the hard spheres (see Table I). The EXP approximation, on the other hand, has the correct low density limit and predicts a  $g_{\alpha\alpha}(r)$  that is always non-negative. Similarly, the ORPA +  $B_2$  results for thermodynamic properties are much more accurate at low concentrations than those derived from the physically incorrect MSM correlation functions.

The important reason why the results of the optimized cluster theory are so accurate is that the optimization condition is used in the choice of perturbation and renormalized potentials. The optimization procedure is much more significant than the specific form of cluster theory which we used. There are several ways of obtaining formally exact infinite series for the properties of fluids, for example the Mayer cluster series<sup>8</sup> and the mode expansion.<sup>9,10</sup> These series can be

partially summed in a variety of ways. For example, chains of perturbation bonds can be summed as in the Mayer ionic solution theory<sup>8</sup>, or generalized chains can be summed as in the  $\gamma$  expansion theory.<sup>11</sup> Finally, these partially summed series can be regrouped in a variety of ways. For example, terms of the same order in the concentration can be grouped together, or the  $\gamma$  ordering or  $\Gamma$  ordering procedures<sup>11</sup> could be used. Each of the resulting series is formally exact and so they are all equivalent to each other. For practical computations, however, an infinite series is useful only if all but a few terms can be neglected without appreciable loss of accuracy. For series which contain renormalized potentials, the optimization condition improves the convergence so well that for many problems the terms of significance can be easily identified and evaluated and the others can be neglected. In this paper we have chosen a series based on the Mayer cluster theory and a summation technique which is suggested by the  $\gamma$  expansion, but results of comparable numerical accuracy could also be obtained using a number of other types of series, provided the optimization procedure is employed.<sup>12</sup>

The advantage of using an expansion of the form used herein is that all the terms in the expansion are known fairly explicitly. As a result, the significant terms in the series for the free energy and  $g(r)$  can be easily identified (as was done in paper I). In contrast, the successive terms in the mode expansion and the  $\gamma$  expansion are not easily expressed in ways which readily allow one to assess their importance. Thus, accurate theories are easier to obtain with the cluster expansion methods used herein than with some other theories. For example for 2-2 salts at low concentrations, the ORPA +  $B_2$  approximation is more accurate than the optimized mode expansion<sup>10</sup> truncated after the two-mode term, because the higher mode terms contain contributions which are significant but which are difficult to obtain in simple form.

### III. Simple Liquids

In this section we consider the Lennard-Jones fluid. The total potential energy is a sum of pair potentials of the 6-12 type. Specifically, the two-particle interaction is

$$w(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6] , \quad (3.1)$$

where  $\epsilon$  and  $\sigma$  are constants with the units of energy and length, respectively.

The analysis of this fluid begins with the separation of the potential into a reference part,  $u_0(r)$ , and a perturbation  $u(r)$ . Since it is desirable<sup>13,14</sup> for the reference potential to be harshly repulsive (i.e., the Mayer  $f$ -function for  $u_0(r)$  should closely resemble the  $f$ -function for a hard sphere potential), and since it is also desirable for the perturbation to be a slowly varying function of position, a very convenient choice for  $u_0(r)$  and  $u(r)$  is

$$\begin{aligned} u_0(r) &= w(r) + \epsilon , & r \leq 2^{1/6} \sigma , \\ &= 0 , & r > 2^{1/6} \sigma , \\ u(r) &= -\epsilon , & r \leq 2^{1/6} \sigma , \\ &= w(r) , & r > 2^{1/6} \sigma . \end{aligned} \quad (3.2)$$

The sum  $u_0(r) + u(r)$  is  $w(r)$ . The reference potential contains all the repulsive forces in  $w(r)$  and no other forces. The perturbation contains all the attractive forces. The motivation for this particular separation of  $w(r)$  is discussed in more detail by the authors in previous publications.<sup>13,14</sup>

Since the reference interaction is not a hard core repulsion, the optimization method developed in paper I is not directly applicable to the Lennard-Jones system. As a result, it is convenient to introduce the trial system in which the pair potential is

$$w_T(r) = u_d(r) + u(r) . \quad (3.3)$$

[The subscript "T" is used to denote properties of the trial system.]

The optimized cluster expansion methods can be used to predict the properties of the fluid with the pair potential  $w_T(r)$ . Once these properties are known, the properties of the Lennard-Jones fluid are straightforwardly obtained through the application of a type of cluster expansion<sup>15</sup> (which we have called the "blip function" expansion). The formulas needed to arrive at the Lennard-Jones properties from the trial properties are given in Eqs. (11)-(14) of Ref. 14.

We have used the EXP approximation for  $g(r)$  [Eq. (5.7) of I] to calculate  $g_T(r)$ ; and then with the blip function expansion we determined  $g(r)$  for the Lennard-Jones system. The hard sphere radial distribution function,  $g_d(r)$ , is needed to perform these computations. This function has been expressed in convenient analytic form by Verlet and Weis,<sup>16</sup> and we use their expressions. The optimization condition, Eq. (4.1) of I, is solved numerically using the calculational procedure outlined in Section III of Reference 13. Some of our results are graphed in Figs. 3 and 4 and tabulated in Tables III and IV. These results are compared with those obtained from Verlet's molecular dynamics experiments.<sup>17</sup> Also shown for comparison are the predictions of the high temperature approximation<sup>13</sup> (HTA) and the optimized random phase approximation<sup>14</sup> (ORPA).

The results in Figure 3 and Table III describe a state which is near the critical temperature but at a density slightly higher than critical. Figure 4 and Table IV concern a high density, low temperature state near the triple point. It can be seen that the HTA, ORPA, and EXP results represent a sequence of approximations that converge very quickly to the correct answer and that the accuracy of the EXP approximation is excellent.

#### IV. Concluding Remarks

The results tabulated and graphed above demonstrate the accuracy of the approximations developed in paper I and generalized in II. It is seen that the ORPA +  $B_2$  and EXP approximations are capable of treating fluids in which the traditional perturbation parameters are large. While these approximations are rigorously exact for low densities and/or weak interactions, our results show that they remain accurate when the density is large, when the strength of the perturbation interaction is large, and when the range of the interaction is large. Thus, the ORPA +  $B_2$  and EXP approximations provide a comprehensive theory of classical fluids -- a theory which is useful for many classes of systems. Further, the approximations are computationally simple to use. The features of wide applicability and simplicity have motivated us to employ these same methods (along the lines of paper II) to study liquid water. This investigation is the subject of a future paper.

Acknowledgements

We are grateful to John P. Valleau for permission to use some of his unpublished Monte Carlo calculations on 2-2 ionic solutions. One of us (J.D.W.) thanks K. E. Shuler for his hospitality and support at the University of California, San Diego.

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\* Work supported by the National Science Foundation, the donors of the Petroleum Research Fund as administered by the American Chemical Society, and the U. S. Department of Defense administered by the Office of Naval Research (Grant N00014-69A-0200-6018).

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12. The contrast between optimized and unoptimized theories is easily seen by considering the free energy series for symmetric primitive model electrolytes. If perturbation ring diagrams are summed, as in Mayer's work (Ref. 8), and if generalized chains are summed, as in the work of Stell and Lebowitz (Ref. 11), and if the one-mode term in the mode expansion is evaluated (Ref. 9), exactly the same formulas are obtained in each case for this particular model of electrolytes. If the perturbation potential is not optimized, i.e. if it is assumed to be purely Coulombic for all distances, these formulas give the Debye-Hückel result, which is known to be quantitatively and qualitatively incorrect for ionic solutions of about 1M. If the perturbation potential is optimized, however, the ORPA (optimized random phase approximation) is obtained, which is much more accurate (see Ref. 10).
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Table I. Comparison of Radial Distribution Functions at Contact for a 1-1 Symmetric Primitive Model Aqueous Electrolyte Solution.<sup>a</sup>

<sup>c</sup> b	(g <sub>+-</sub> ) <sup>c</sup> <sub>MC</sub>	(g <sub>+-</sub> ) <sub>MSM</sub>	(g <sub>+-</sub> ) <sub>EXP</sub>	(g <sub>++</sub> ) <sup>c</sup> <sub>MC</sub>	(g <sub>++</sub> ) <sub>MSM</sub>	(g <sub>++</sub> ) <sub>EXP</sub>
.00911	5.22±.40	2.49	4.43	.270±.068	-.486	.226
.1038	3.25±.07	2.20	3.32	.319±.012	-.175	.309
.425	2.62±.04	1.99	2.68	.418±.018	.118	.413
1.000	2.23±.05	1.90	2.45	.505±.27	.358	.522
1.968	2.38±.07	1.93	2.45	.706±.028	.631	.669

- a. For these calculations, the ionic diameter is 4.25 Å, the dielectric constant of the solvent is 78.5, and the temperature is 298°K. Here g<sub>+-</sub> is the pair correlation function at contact for ions of different charge, and g<sub>++</sub> is the same quantity for ions of the same charge. MC denotes Monte Carlo results of Card and Valleau (Ref. 4). MSM and EXP denote the mean spherical model and EXP approximations, respectively.
- b. The salt concentration in moles per liter.
- c. Monte Carlo results for 200 ions.

Table II. Excess Internal Energy for a 2-2 Symmetric Primitive Model Aqueous Electrolyte Solution.<sup>a</sup>

$c^b$	$-\Delta E/2Nk_B T$			$\Delta^f$
	ORPA <sup>c</sup>	ORPA + B <sub>2</sub> <sup>d</sup>	MC <sup>e</sup>	
.0625	1.46	2.02	1.893 $\pm$ .017	.13
.250	2.18	2.55	2.473 $\pm$ .019	.08
.5625	2.64	2.90	2.822 $\pm$ .008	.08
1.000	2.98	3.19	3.091 $\pm$ .011	.10
2.000	3.38	3.57	3.509 $\pm$ .016	.06

- a. In this model, the ionic diameter is  $4.25 \text{ \AA}$ , the dielectric constant is 78.358 and it is temperature independent, the temperature is 298.16°K. The quantity  $\Delta E$  is the configurational internal energy of the ions and  $2N$  is the total number of ions.
- b. Salt concentration in moles per liter.
- c. Obtained from differentiation of the ORPA for the free energy. For symmetric primitive model electrolytes, the energy equation applied to the MSM gives identical results.
- d. Obtained from differentiation of the ORPA + B<sub>2</sub> approximation for the free energy.
- e. Monte Carlo predictions (Ref. 4).
- f. Difference between the ORPA + B<sub>2</sub> and Monte Carlo results.

Table III. Comparison of Radial Distribution Functions for the Lennard-Jones Fluid for  $\rho^* = .50$  and  $T^* = 1.36$

$r/\sigma$	$g_{HTA}(r)^a$	$g_{ORPA}(r)^b$	$g_{EXP}(r)^c$	$g_{MD}(r)^d$	$\Delta^e$
0.840	0.000	0.000	0.000	.000	.000
0.880	0.001	0.001	0.001	.001	.000
0.920	0.053	0.054	0.054	.059	.015
0.960	0.404	0.411	0.420	.428	.008
1.000	1.055	1.087	1.128	1.109	-.019
1.040	1.579	1.653	1.737	1.694	-.043
1.080	1.770	1.889	2.007	1.961	-.046
1.120	1.713	1.870	2.005	1.946	-.059
1.160	1.583	1.749	1.868	1.830	-.038
1.200	1.468	1.610	1.692	1.658	-.034
1.240	1.368	1.474	1.521	1.491	-.030
1.280	1.280	1.350	1.373	1.335	-.038
1.320	1.204	1.241	1.249	1.227	-.022
1.360	1.139	1.148	1.150	1.129	-.021
1.400	1.083	1.072	1.071	1.059	-.012
1.480	0.996	0.960	0.961	.929	-.032
1.560	0.938	0.894	0.898	.881	-.017
1.640	0.904	0.865	0.869	.860	-.009
1.720	0.892	0.863	0.866	.854	-.012
1.800	0.899	0.883	0.885	.894	.009
1.880	0.923	0.920	0.920	.938	.018
1.960	0.961	0.972	0.972	.994	.022
2.040	1.007	1.029	1.030	1.047	.017
2.120	1.032	1.060	1.062	1.075	.013
2.200	1.040	1.068	1.069	1.073	.004
2.280	1.037	1.056	1.057	1.056	-.001
2.360	1.027	1.037	1.037	1.030	-.007
2.400	1.022	1.026	1.027	1.022	-.005

a. High temperature approximation.

b. Optimized random phase approximation

c. EXP approximation.

d. Molecular dynamics. Ref. 17.

e. The difference between the molecular dynamics result and the EXP approximation.

Table IV. Comparison of Radial Distribution Functions for the Lennard-Jones Fluid for  $\rho^* = .85$  and  $T^* = .88$

$r/\sigma$	$g_{HTA}(r)^a$	$g_{ORPA}(r)^b$	$g_{EXP}(r)^c$	$g_{MD}(r)^d$	$\Delta^e$
0.840	0.000	0.000	0.000	0.000	.000
0.880	0.000	0.000	0.000	0.003	.003
0.920	0.019	0.018	0.014	0.030	.016
0.960	0.445	0.428	0.339	0.412	.073
1.000	1.813	1.750	1.492	1.511	.019
1.040	2.918	2.839	2.599	2.546	-.053
1.080	2.956	2.924	2.855	2.871	.016
1.120	2.432	2.480	2.551	2.594	.043
1.160	1.918	2.013	2.106	2.151	.043
1.200	1.558	1.648	1.705	1.744	.039
1.240	1.290	1.356	1.378	1.386	.008
1.280	1.083	1.119	1.123	1.121	-.002
1.320	0.921	0.931	0.930	0.946	.016
1.360	0.797	0.788	0.790	0.817	.027
1.400	0.710	0.686	0.693	0.742	.049
1.480	0.624	0.590	0.603	0.622	.019
1.560	0.630	0.600	0.611	0.599	-.012
1.640	0.694	0.676	0.681	0.656	-.025
1.720	0.793	0.786	0.788	0.757	-.031
1.800	0.910	0.914	0.913	0.907	-.006
1.880	1.038	1.047	1.047	1.072	.025
1.960	1.172	1.181	1.183	1.198	.015
2.040	1.283	1.293	1.295	1.267	-.028
2.120	1.253	1.270	1.274	1.246	-.028
2.200	1.125	1.143	1.145	1.151	.006
2.280	0.995	1.001	1.001	1.021	.020
2.360	0.901	0.893	0.894	0.923	.029
2.400	0.875	0.862	0.864	0.881	.017

a. High temperature approximation.

b. Optimized random phase approximation.

c. EXP approximation.

d. Molecular dynamics. Ref. 17.

e. The difference between the molecular dynamics result and the EXP approximation.

Figure Captions

Figure 1. Pair-correlation functions for a 1-1 symmetric primitive model aqueous ionic solution. The ionic diameter is  $4.25 \text{ \AA}$ , the dielectric constant of the solvent is 78.5, and the temperature is  $298^\circ\text{K}$ . The salt concentration is .00911 M. The points are the results of Monte Carlo calculations (Ref. 4) for 200 ions. The curves are the results of the EXP approximation. The upper and lower sets of results correspond to the function for unlike and like charged species, respectively.

Figure 2. Pair-correlation functions for a 1-1 symmetric primitive model aqueous ionic solution. Triangular and circular points are Monte Carlo results for .425 M and 1.986 M, respectively, and the smooth curves are the exponential approximation results. See the caption of Fig. 1 for additional details.

Figure 3. Pair-correlation functions for the Lennard-Jones fluid for a state near the critical point. The open circles are molecular dynamics results (Ref. 17). The dashed, dotted, and solid curves are the results for the high temperature approximation, the optimized random phase approximation, and the EXP approximation, respectively.

Figure 4. Pair-correlation functions for the Lennard-Jones fluid for a state near the triple point. See caption of Fig. 3 for additional information.

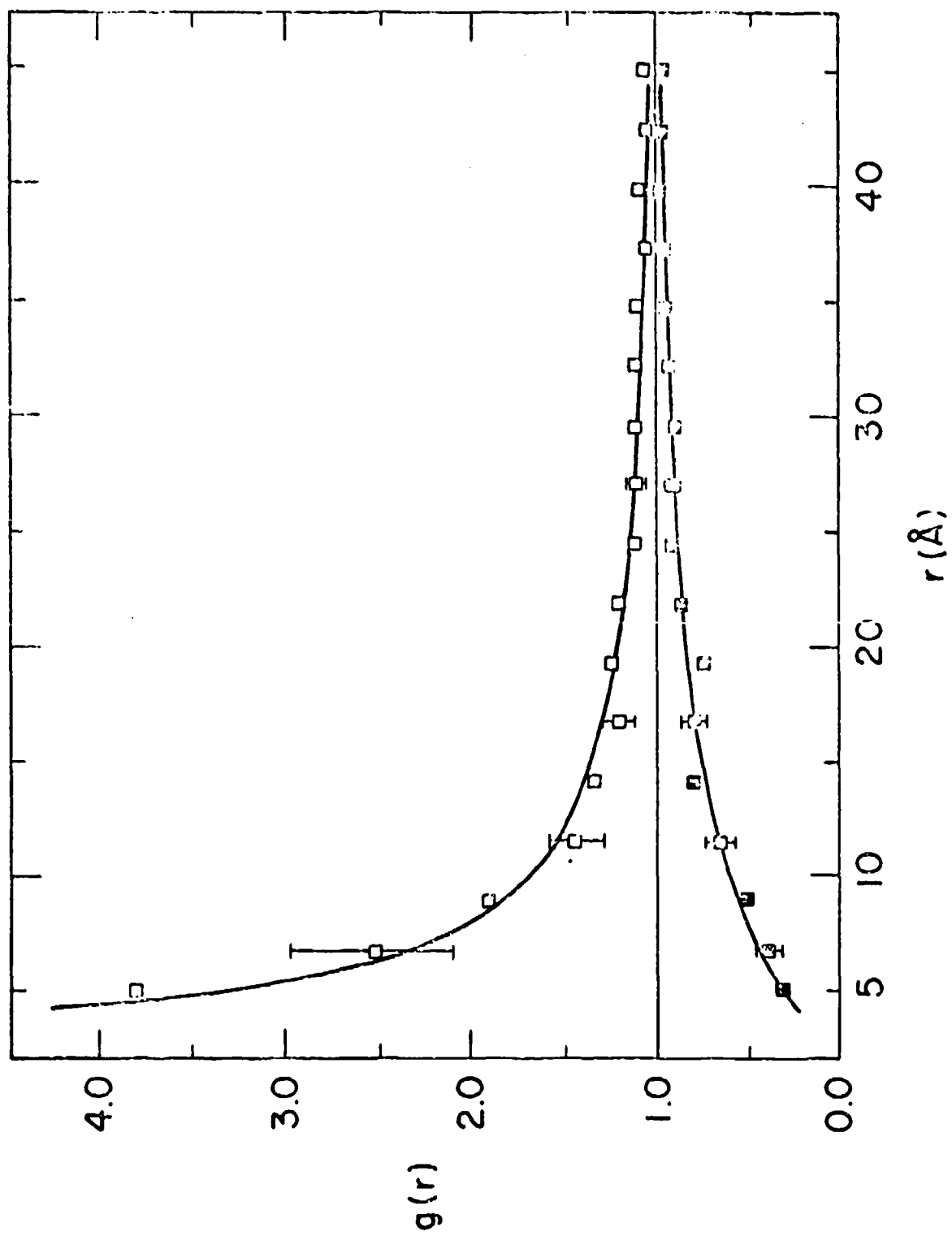


Figure 1

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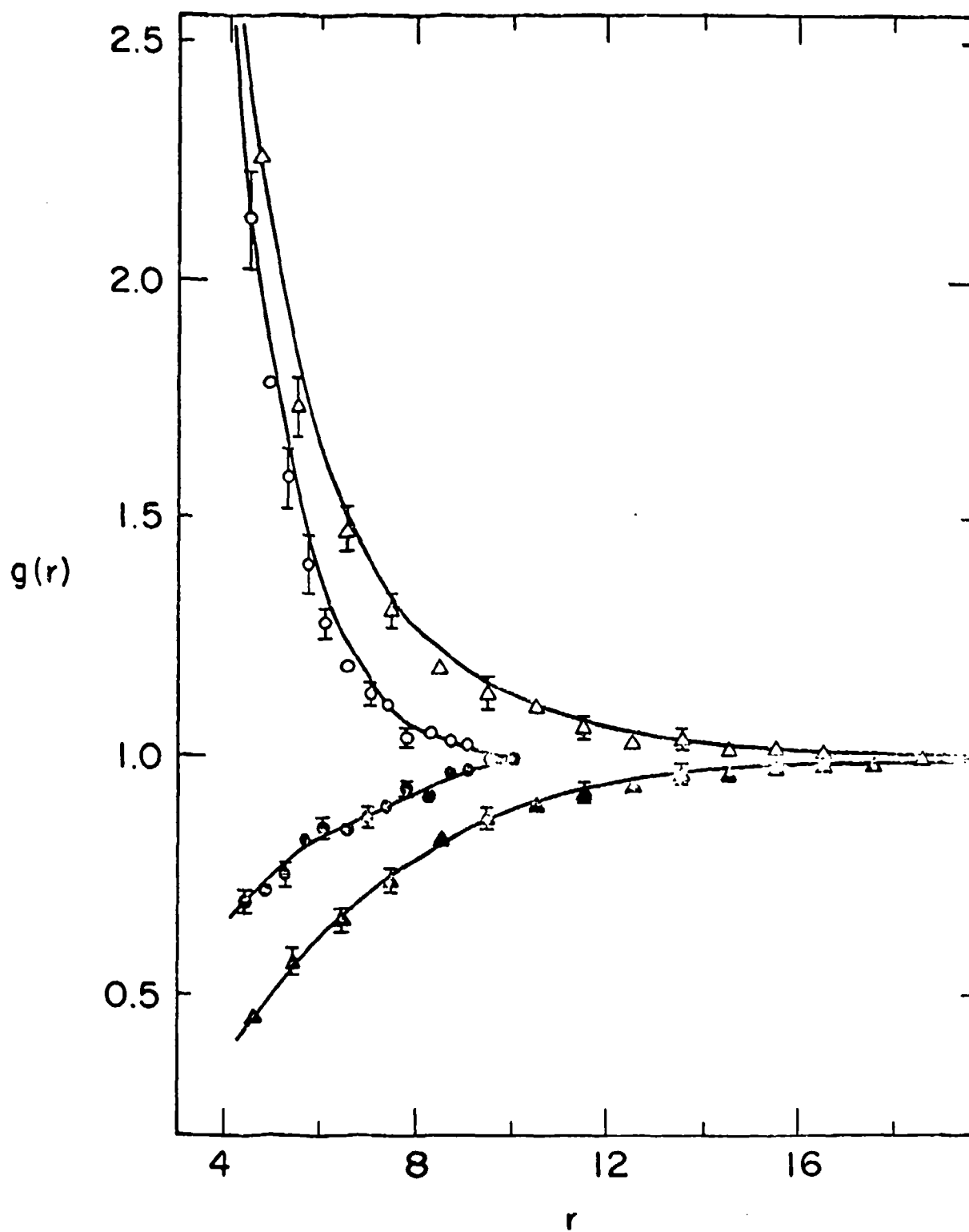


Figure 2

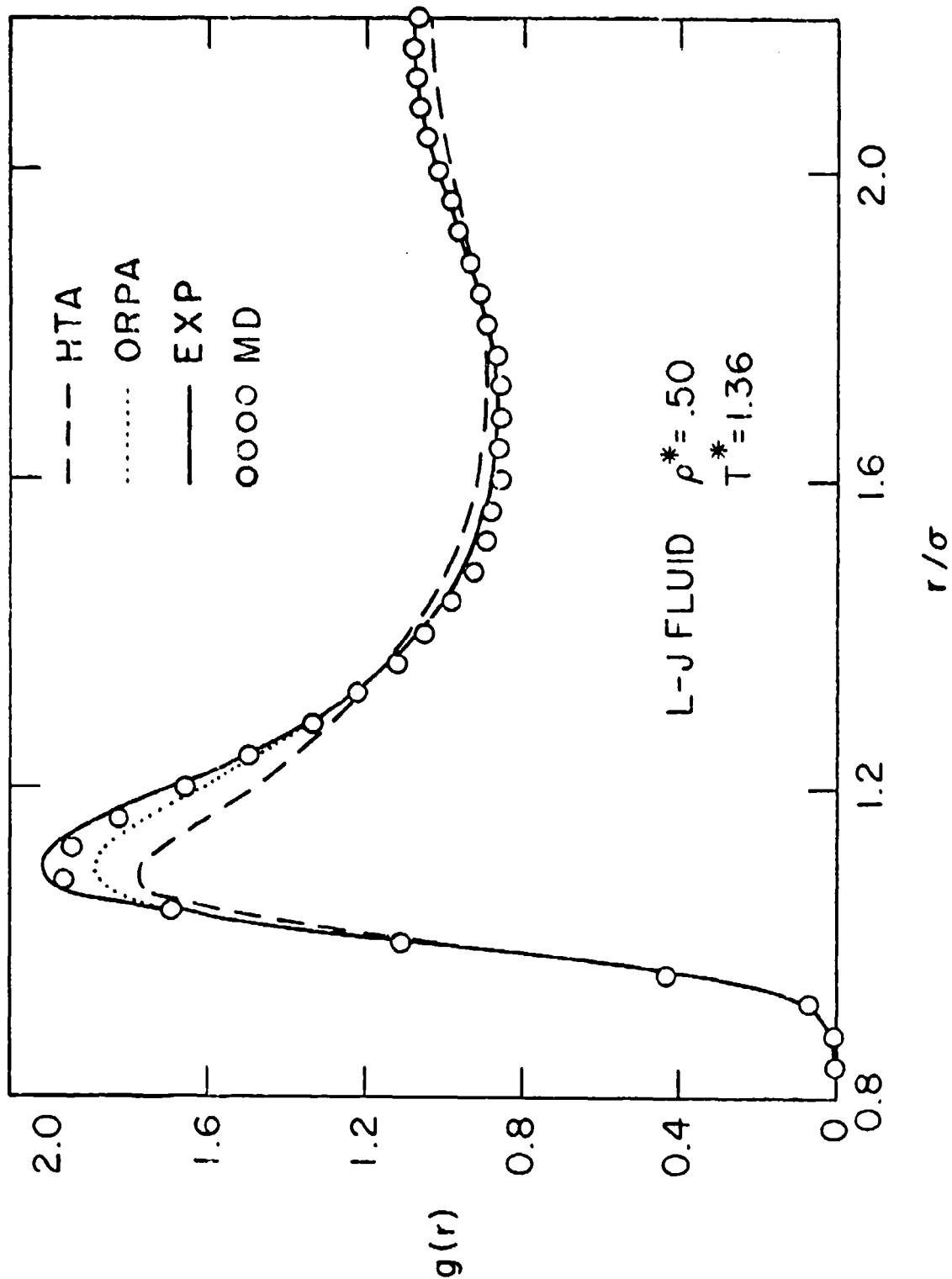


Figure 3



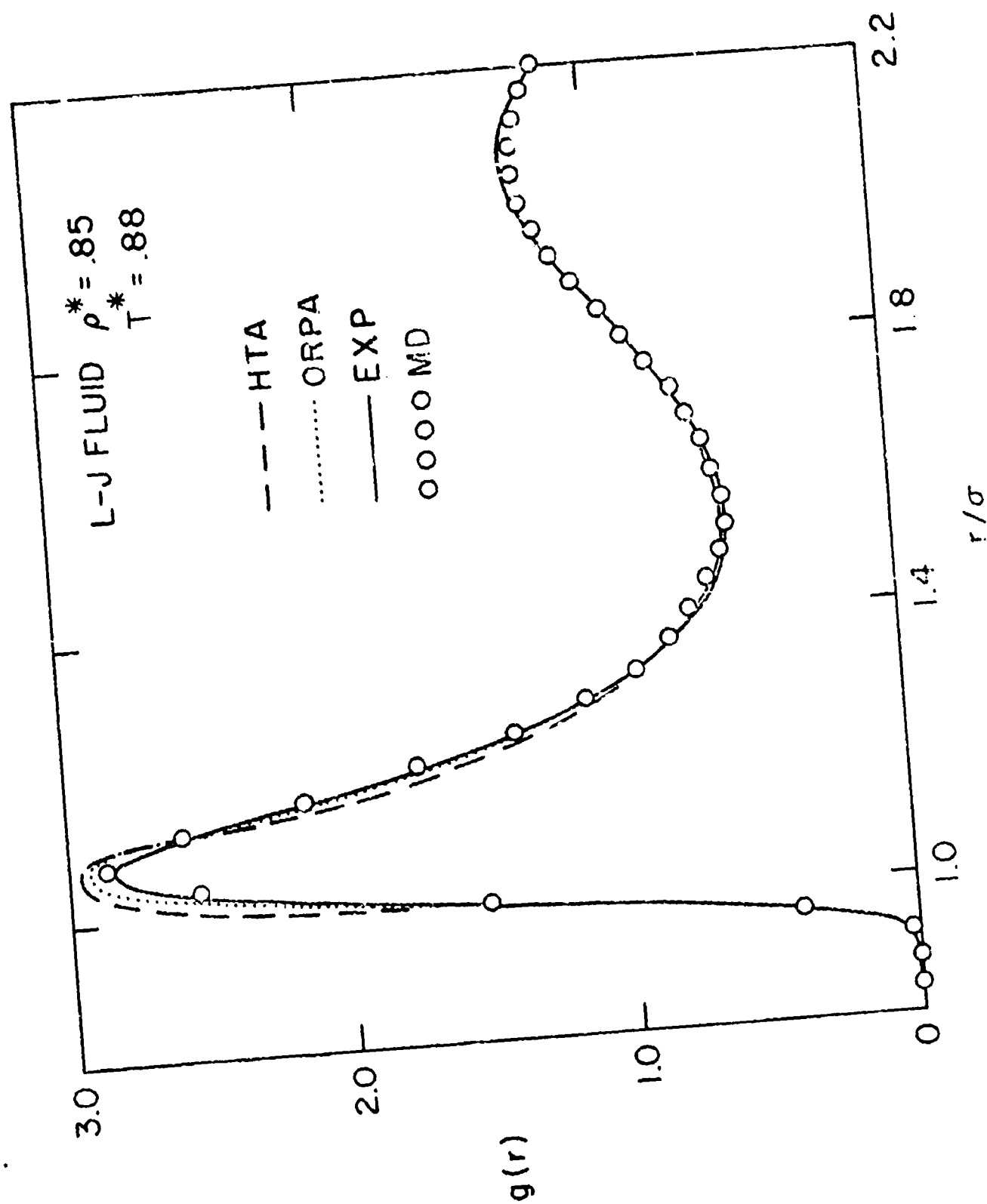


Figure 4